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Liquid Crystal Polymers:

Thermotropic Rigid Aromatic Copolyesters with Bisphenol Spacers

by

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ABSTRACT

A series of aromatic polyesters based on either poly(chloro-p-phenylene terephthalate) or poly (methyl-p-phenylene terephthalate) modified by incorporation of various amounts of bisphenols of different structures were prepared and their thermotropic liquid crystal properties were studied by several methods including: (1) visual observation of stir-opalescence of the polymer melts,(2) examination of melt birefringence on a polarizing microscope, (3) studies of small angle light scattering characteristics, and (4) characterization by wide angle x-ray diffraction. It was found that the steric effects of non-linear bisphenol modifiers were the most important factors in controlling the liquid crystallinity of the resulting copolyesters.
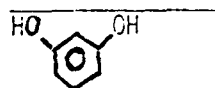
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INTRODUCTION

One of the most interesting recent developments in polymer chemistry
is the observation of liquid crystallinity in aromatic polyesters and
polyamides. For the aromatic polyamides, liquid crystallinity is observed
in solutions of the polymers in specific solvents and can be referred to
as a lyotropic behavior[1-4]. In contrast, the aromatic polyesters show
thermotropic behavior because liquid crystallinity occurs in the melt
within a specific temperature range[5-8]. In both cases the liquid cry-
stallinity is of the nematic type, indicating that the rod-like polymer
chains exist in an approximately parallel array but not lined up end-to-
end. That is, there is a two-dimensional but not a three-dimensional
order in the liquid crystalline phase and the placement of the mesogenic
unit occurs randomly within the parallel array of molecules within this
phase.

These types of polymers offer great potential in the combination
of ease of processability with superior mechanical properties of strength
and stiffness. However, very little information has been reported in the
literature on the relationship between polymer structure and properties
in such systems. Toward this end, a systematic investigation is being
carried out in this laboratory on the effect of variations in composition
of aromatic copolyesters on their liquid crystalline behavior and on their
resulting rheological and mechanical properties. The specific systems
to be discussed in this report are based on copolyesters of either chlo-
rohydroquinone, CHQ, or methylhydroquinone, MHQ, with terephthalic acid,
TPA, both of which are known to form nematic melts[7]. The copolymers
studied contained a series of bisphenols which were selected to determine
the effect of copolymer structure and composition on the thermotropic

behavior . The bisphenols examined for this purpose had the following general molecular structure:
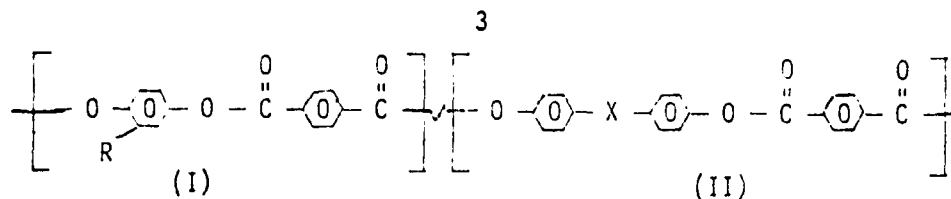
$$HO-\langle O \rangle - X - \langle O \rangle - CH$$

X	Symbol	Trivial Name
(none)	BP	biphenol
$C(CH_3)_2$	BPA	bisphenol A
CH_2	BPM	bisphenol methane
O	ODP	oxydiphenol
S	TDP	thiodiphenol
SO_2	SDP	sulfonyldiphenol
CO	DPB	dihydroxybenzophenone

HO—〈O〉—OH	RES	resorcinol

As shown in the table, resorcinol was also included in addition to the parasubstituted bisphenols. Some preliminary results of the present study have already been described[9].

RESULTS AND DISCUSSION

Synthesis and General Properties of Poly(chloro-p-phenylene terephthalate) and Copolyesters Containing Bisphenol Units.

A series of aromatic copolyesters having chloro-p-phenylene terephthalate (I,R = Cl) and various bisphenol terephthalate (II) units as described above were synthesized in a range of comonomer compositions varying, in general, from 10 to 70 mole % of the bisphenol in 10 or 15 mole % increments, see Tables 2-8. The overall range of compositions for each bisphenol is summarized in Table 1.

$$\left[\!-O-\overset{R}{\underset{}{\bigcirc}}-O-\overset{O}{\overset{\|}{C}}-\bigcirc-\overset{O}{\overset{\|}{C}}-\right] \text{(I)} \quad \left[\!-O-\bigcirc-X-\bigcirc-O-\overset{O}{\overset{\|}{C}}-\bigcirc-\overset{O}{\overset{\|}{C}}-\right] \text{(II)}$$

In general polymer yields were high and the copolymer compositions were essentially the same as the monomer compositions as shown in Tables 2 through 8. All of the polyesters in Tables 1-8 were insoluble in the reaction medium and precipitated out as they were formed during polymerization before reaching high molecular weights. As a result, their molecular weights were not expected to be very high, and this expectation is reflected by the relatively low solution viscosity numbers obtained for all samples. Poly (chloro-p-phenylene terephthalate), the homopolymer from chlorohydro-quinone and terephthalic acid of Table 2, which had an inherent viscosity as measured in trifluoromethanesulfonic acid of 0.382, could not be characterized for molecular weight by light scattering methods so it must have had a molecular weight well below 10,000, but no absolute value is as yet available.

The melting points of the copolymers as determined by DSC were usually much less well defined than those of the homopolymers with broad and small melting endotherms, especially for the compositions containing from 40 to 60 mole % of the bisphenol comonomers. This result is understandable because these copolyesters would be expected to either have low degrees of crystallinity or to be completely amorphous. The exceptions were the CHQ/TDP copolymers of Table 5, which showed sharp and well defined melting behaviors by DSC analysis even in this composition range. The melting point of 340°C reported in Table 2 for the CHQ homopolymer may be depressed because the polymer was apparently of quite low molecular weight.

This polymer showed a very broad and shallow endotherm extending from about 360°C to the upper limit for the DSC analysis of 400°C which is presumably associated with the transition from the liquid crystal state to the isotropic melt; that is, with the clearing temperature.

Copolymerization with small amounts of the bisphenol monomers initially depressed the melting points as expected, but at higher compositions the melting points either increased or continued to decrease depending on the type of comonomer. In the range of compositional variations of the present study, the CHQ/BP and CHQ/ODP copolyesters were examples of the former type of copolymers while the CHQ/BPM copolymers were of the latter type. All the melting temperatures reported in the table were obtained on unannealed samples of the as-prepared polymers.

All copolymers containing 85 mole% or more of the chlorohydroquinone units and all of the CHQ/BP copolymers of Table 7 were soluble at room temperature in trifluoromethanesulfonic acid, and all of those containing lower amounts of chlorohydroquinone units were soluble in p-chlorophenol. The polymer solutions in trifuluoromethanesulfonic acid had colors ranging from light green to brown and the colors deepened with time. Because of the extremely high acidity of this acid[10], it is likely that protonation and even degradation could be responsible for these colored solutions. The solution viscosities of the BP copolymers of Table 7 were much lower than those of the other copolyesters. In most cases, because of slow rates of dissolution, at least 20 hours of contact time between the solvent and the polymer was required before viscosity measurements could be made and, in these strong acid solvents, hydrolytic degradation of the polymers could have occurred to lower their molecular weights.

Synthesis and General Properties of Copolyesters Derived from Methylhydroquinone and Bisphenols.

A second series of copolyesters were prepared based on methylhydro-
quinone (MHQ, R = CH_3 in I) instead of chlorohydroquinone with the results
shown in Tables 9 and 10. Poly (methyl-p-phenylene terephthalate) had a
higher melting point, 371°C, than that of the chlorohydroquinone polymer, 340°C.
As can be seen from the data in Table 9, the copolymerization of MHQ with
BPA (for example, note the copolymer of 85/15 mole ratio) did not depress
the melting temperature of the polyester even though the degree of crystallini-
ty was apprarently drastically reduced. However, the homopolymer melting
point may well have been abnormally low because the molecular weight of this
polymer was apparently quite low. Unlike all other copolyesters investigated
in this study, at the 70/30 mole ratio, the MHQ copolyesters with BPA did
not show a melting endotherm and it appeared that the crystallinity was com-
pletely destroyed. These copolyesters showed better solubility than CHQ
copolymers and could be dissolved in a 60 phenol/40 tetrachlorethane (w/w)
mixture as well as in p-chlorophenol. The copolymer prepared from an equimolar
mixture of MHQ and BPA was fairly soluble even in tetrachlorethane at room
temperature.

A series of copolyesters was prepared from equimolar amounts of MHQ with
most of the bisphenols investigated in the series of CHQ copolyesters with
the results summarized in Table 10. In this series, polymer yields were high,
ranging 88 to 98.5%, and the inherent viscosity numbers were in the range of
0.4 to 0.67. The melting endotherms observed on the DSC thermograms were
rather broad for all of these copolymers with the exception of those from DBP
and from TDP. In this series BPM seemed to be most effective in lowering
the melting points of the resulting copolyesters. This result can probably
be attributed to the combination of the low polarity and the flexible nature
of the methylene substituent between the two phenolic rings. The 50/50 BPA

copolymer did not show a melting endotherm in the DSC thermogram, while the 50/50 BP copolymer of Table 10 showed an extremely broad melting endotherm, and the melting point of this copolymer could not be properly defined.

All of the copolymers in Table 10, except the BP copolyester, were completely soluble in p-chlorophenol, but they were only partially soluble in the 60/40 phenol/tetrachlorethane mixture. The BP copolymer was soluble in trifluoromethanesulfonic acid.

Anisotropic Liquid Crystal Polymer Melts.

Thermotropic liquid crystalline phases have turbid melts and exhibit anisotropic properties such as birefringence and light scattering[11-14]. A particular characteristic is the observation of stir-opalscence of these anisotropic melts. The polyesters prepared in this investigation were examined visually for the occurrence of stir-opalescence in the melts.

From observations on stir-opalescence of polymer melts, attempts were made to qualitatively describe the intensity for each copolymer composition as reported in the tables. With the exception of the BP copolymers, all of the copolyesters showed a gradual reduction in the intensity of stir-opales-cence as the content of the bisphenol comonomer was increased. Copolymeri-zation with all of these bisphenols markedly decreased the abilities of the polymers to form into anisotropic liquid crystal states. Another important observation made was that some of the polymers, for example the 60 CHQ/40 RES and 40 CHQ/60 RES copolyesters in Table 8, the 70 MHQ/30 BPA copolyester in Table 9, and the 50 MHQ/50 BP copolyester in Table 10, all of which showed essentially no crystalline melting transitions on DSC and presumably are mainly amorphous in nature, exhibited stir-opalescence. This observation indicated that even apparently amorphous linear polyesters can form liquid crystal states above their glass transition temperatures if the structure of the polymers favors the parallel alignment of the polymer chains in the melt. The liquid crystal states of these polyesters could easily be quenched and supercooled to room temperature.

Ringsdorf and coworkers[15] recently observed a similar phenomenon for liquid crystalline polymers having polysiloxane flexible spacers in the main chain. These polymers also underwent a phase transitions from the glassy state directly to the liquid crystal states at their softening points.

Because the melting temperatures of the polyesters of the present study were fairly high, microscopic and small angle light scattering studies were conducted at a room temperature on polymer films prepared by quenching their melts at a temperature of about 40°C above the melting point with ice-water. As seen in the photomicrographs of Figure 1, all of the liquid crystalline CHQ/BPA copolyester melts showed a marble texture (compare Figures 1(a) with 1(b), and 1(c))[16], and the 60 CHQ/40 BPA copolyester of Figure 1 showed only a very limited degree of birefringence with large areas of an apparently isotropic phase as indicated by the dark areas in the microphotograph. The 50 CHQ/50 BPA copolyester revealed essentially no anisotropy and did not transmit any cross-polarized light. In these samples, the occurrence of a homeotropic alignment from the 60 CHQ/40 BPA and 50 CHQ/50 BPA copolymers resulting in darkness under cross-polarizers is very unlikely. These observations are in complete agreement with the observed stir-opalescence properties of these polymers as described above. The same comparison was true for all of the copolyesters investigated.

Figure 2 shows the photomomicrographs of two other copolymers which are characterized by a threaded Schlieren texture, a characteristic optical texture of nematic mesophase[16].

Small angle light scattering behavior of polymer films is also used to obtain information on the morphological structure of polymers in the solid state[17,18]. Because it is known that H_v scattering with crossed polars is influenced by structural anisotropy and V_v scattering with parallel polars

by the density fluctuation as well as structural anisotropy[17], only H_v
scattering characteristics of the polymers were measured. The scattering
patterns of some of the polymers are shown in Figures 3 and 4. It can clearly
be seen from these photographs that the intensity of the scattered light
steadily decreased with the content of the nonlinear bisphenol units in the
copolyesters and that it finally became negligible or completely vanished for
the compositions which are believed to form only isotropic, non-liquid crystal
amorphous states. These observations are consistent with the results obtained
fom the microscopy study and from examination of their stir-opalescence.
A ±45° crossed, four-leaf clover shape for the scattering pattern was observed
only for the homopolymer derived from CHQ, while circularly symmetric and
azimuthally independent scattering patterns were obtained for all of the other
liquid crystal compositions. This result suggests that the scattering elements
of these copolyesters are generally spherical in shape and have random orien-
tation correlations. In contrast, the homopolymer from CHQ apparently had a
superstructure consisting of rigid rod assemblies.

The small angle light scattering characteristics of various liquid states
of many low molecular weight compounds and of some polymers have been repor-
ted[19-21]. Even though theoretical interpretation of the scattering phenomena
by the liquid crystal mesophases requires much more study, this method certainly
provides very useful information when the size of anisotropic domains are in
the range of the wavelength of visible light or about 1000 ~ 10000 A°. As
demonstrated by us[22] and others[21], this method could be used also to follow
directly the phase transition from the liquid crystal state to isotropic state
provided that the transition temperature is not too high and is below the de-
composition temperature of the polymers. For the present series of polyester,

however, the transitions from the mesophase to the isotropic phase could not
be followed by this method because the polymers underwent thermal decomposition
before the transition to the isotropic melt.

The wide angle x-ray diffraction patterns of the liquid crystal state
(quenched melt films) of some of the polymers examined were basically the same
as those expected for nematic states[23]. As shown in Figure 5, the diffraction
pattern of the polymer melt of the 70 CHQ/30 ODP copolyester of Table 4, ex-
hibited a broad and weak inner ring and a stronger diffuse ring at a larger
angle ($2\theta = 20.3°$). The interplanar distance between parallel polymer chains
in the nematic state as deduced from this value of 2θ using the De Vries'
modification[23,24] of the Bragg equation was 4.8 A°. Other liquid crystal
compositions prepared in this investigation, for example the CHQ/bPA copolyesters,
also showed interplanar spacings of approximately 4.7-5.0 A°. In general,
inclusion of higher amounts of nonlinear bisphenol comonomers tended to
increase the interplanar distance. Further x-ray studies of these polymers
are in progress.

The melt viscosity of a liquid crystal
melt is known to be, in general, much lower than that of an isotropic melt
for polymers of the same molecular weight. In the present work, the observa-
tion of stir-opalescence of polymer melts between two microscope cover glasses
on a Fisher-Johns melting point apparatus permitted at least a highly qualita-
tive conclusion that the liquid crystal melts were indeed much less viscous
than the isotropic melts of nonliquid crystalline polymers, and movement of
the top microscope cover glass was much easier with the liquid crystal melts
than with the isotropic melts. Further study on the melt rheology of these
polymers in relation to their structure and composition, which is presently

in progress in this laboratory, is expected to give a more detailed picture
on the relationship between melt behavior and polymer structure.

Dependence of Liquid Crystallinity of Linear Aromatic Polyesters on Their
Structure.

By considering all the characterization results reported here for chloro-
hydroquinone copolyesters, we can arrive at some semi-quantitative conclusions
about the maximum or threshold amount of each of the bisphenol comonomers
which can be incorporated into the copolymers without complete destruction
of the liquid crystal nature of the resulting copolymers. With the exception
of the biphenol copolymers (x is a direct covalent bond), all of the
copolymers consisted of random arrangements of linear chloro-p-phenylene tere-
phthalate units (I) with non-linear ester units (II) derived from the bi-
sphenols and terephthalic acid.

The differences in the degree of non-linearity or bending caused by the
presence of the middle substituents, x, between the two phenolic rings of
the bisphenol monomers were all within about a 5° angle, which indicates that
the degree of molecular bending caused by these substituents was approximately
the same. The bond angles around the center atoms of the substituents ranged
from about 105° to 110°C. The differences in relative sizes of the substituents,
however, were much greater, and it is to be expected that the larger group
(e.g. - $C(CH_3)_2$ - and -SO_2-) caused increased separation of the parallel
polymer chains to destabilize the nematic mesophase[9,25]. This expectation
was borne out by the observations made in the present study as summarized
in Table 11, which clearly shows that the greater the bulkiness of the middle
substituent in the bisphenol unit, the lower the threshold comonomer amount

which could be accommodated in the copolymer without completely los... ...

liquid crystalline characteristics.

The copolymers of CHQ and RES were unique in that the re... ...

unit does not have a middle substituent, as in bisphenols, and is a... ...

maintain the rigidity of the polymer chain, but its presence ...

of 120° along the backbone of the polymer chains destroying the lin... ...

Again, this non-linearity is expected to reduce the parall... asso...

of the polymer chains in the nematic state and, thereby, to decrea..

stability of mesophase. Copolyesters of MHQ/BPA (Table 9) and of ...

with other bisphenols (Table 10) showed a similar structural depen...

their liquid crystallinity on the type and amount of the bispheno.s ...

merized.

The stereogeometry or space-filling characteristics of polymer mol...

cules and the bulkiness of substituents are considered to be the two m...

important factors in controlling the liquid crystalline characteristics ...

thermotropic, liquid crystalline, aromatic polyesters investigated here

The electronic or polar effects of the substituents on the liquid cryst... ...

properties was not as clear as the steric effects and seemed to be rel...

minor in comparison.

McFarlane and coworkers[6] studied the thermotropic liquid crystal ...

perties of polyesters based on p-oxybenzoate modified PET. They also

corporated into their polymers various nonlinear bisphenols, such as B...

and SDP, as well as non-linear dicarboxylic acid, such as isophthalic ...

They found that the inclusion of 30 mole % of either BPA or SDP could co..

pletely destroy the liquid crystallinity of the base polymer. Replaceme...

of the linear p-oxybenzoate units with the equivalent non-linear m-oxybe...

units (which impart a bending angle of 120° to the backbone) also lead t...

non-liquid crystalline or isotropic compositions. These observations were also attributed to the changes in geometry of the polymer chains caused by the presence of the non-linear comonomer units. It is to be expected that the liquid crystallinity of p-oxybenzoate-modified PET would be destroyed more easily by the presence of small amounts of non-linear bisphenols than for the aromatic polyesters of the present study because p-oxybenzoate-modified PET has non-mesogenic ethylene glycol units, which can also disrupt the mesophase.

CONCLUSIONS

It has been demonstrated that the thermotropic liquid crystalline properties of the aromatic polyesters derived from terephthalic acid and either methylhydroquinone or chlorohydroquinone copolymerized with varying amounts of different bisphenols were greatly dependent upon both the structure and amount of the non-linear comonomer units or "spacers". The non-linear bisphenol spacers containing large or bulky central substituents between the two phenolic rings were found to be more effective in destroying the liquid crystal properties of the resulting copolyesters than those with smaller substituents. Hence, it was concluded that the geometric and steric effects imparted to the polymer chain backbones by the comonomers were the most important controlling factors affecting the liquid crystallinity of the aromatic copolyesters.

EXPERIMENTAL SECTION

Preparation of Polyesters. All of the polyesters were prepared at room temperature by the reaction of an aromatic diol mixture with terephthaloyl chloride in a mixture of 1,1,2,2-tetrachloroethane and pyridine. Detailed

procedures were described in an earlier paper[9].

Characterization of Polymers. Inherent viscosities of polymers were determined using a Cannon-Ubbelhode type viscometer. The thermal properties were measured under a nitrogen atomsphere on a Perkin-Elmer DSC-1B with a heating rate of 20°C/min. The temperature of endotherm maximum was taken as the melting point of the polymer.

Visual observation of stir-opalescence of polymer melts was made as follows: a small amount of the polymer sample was placed between two microscope cover glasses on a Fisher-Johns melting point apparatus and heated rapidly to the melting temperature, which had been predetermined by DSC. The heating rate was then reduced to about 20°C/min., and the top cover glass was moved back and forth with a micro-spatula while the occurrence of stir-opalescence was visually observed with a magnifying glass attached to the apparatus. Continuous observations were made up to the decomposition temperature of polymers.

For microscopy and small angle light scattering studies, a small amount of the polymer sample was placed between two microscope cover glasses on a Fisher-Johns apparatus, which had been preheated to a temperature of 40-50°C above the polymer melting point. After the sample melted completely, the melt was rapidly quenched in an ice-water bath and the sample was stored at low temperature. The thickness of the quenched melt films was generally in the range of 10-25mμ. The optical texture of the samples was studied using a microscope (Leitz, Ortholus model) equipped with a pair of cross-polarizers. The small angle light scattering characteristics of the samples were examined by a He-Ne (λ = 6328 A°) laser fitted with a red filter on an optical bench with a pair of cross-polarizers. The scattering pattern

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was photographed using Polaroid type 52 or 57 films. A 1mm pinhole
was placed behind the sample. The sample to film distance was 32-35 cm.

Samples for x-ray analysis were prepared in a different manner. The
polymer powder (about 0.5g) was spread inside a boat made of aluminum
foil coated with polyetrafluoroethylene (du Pont "Teflon") and the boat
was floated on a salt bath, which was preheated to about 50°C above the
melting temperature of the polymer. When the sample was completely melted,
the boat was removed from the bath while liquid nitrogen was poured into
it. The quenched polymer was pressed at a room temperature into a thin
(~0.5mm) round pellet, which was used for x-ray analysis at room tempera-
ture. The original polymer powders were also pressed into thin pellets
for x-ray analysis. The pelletized samples were affixed to the sample
holder in an x-ray machine for a 16 to 30 hour exposure.

ACKNOWLEDGEMENT

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TABLE 1. Types and Amounts of Bisphenol Monomers
Used to Prepare Aromatic Copolyesters:

$$\text{HO-}\langle\bigcirc\rangle\text{- X -}\langle\bigcirc\rangle\text{- OH}$$
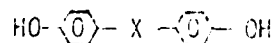
X	Abbreviation	Composition Range, mole%
$-C(CH_3)_2-$	BPA[1]	0 ~ 50
$-CH_2-$	BPM[2]	30 ~ 70
$-O-$	ODP[3]	30 ~ 70
$-S-$	TDP[4]	30 ~ 60
$-SO_2-$	SDP[5]	15 ~ 60
-	BP[6]	30 ~ 70
$\langle\bigcirc\rangle$	RES[7]	15 ~ 70

1. Bisphenol A   2. Bis(4-hydroxyphenyl) methane   3. 4,4"-Oxydiphenol

4. 4,4'-Thiodiphenol   5. 4,4'-Sulfonyldiphenol   6. Biphenol

7. Resorcinol

TABLE 2. Synthesis and Properties of CHQ/BPA Copolyesters

Monomers/Moles CHQ/BPA	Yield, wt.%	Polymer Chlorine Content, wt%		η_{inh}*	M.P.,°C	Stir-Opalescence
		Calcd.	Found			
100/0	97.6	12.9	12.9	0.384	340	very strong
90/10	98.9	11.3	11.5	0.453	347	very strong
70/30	92.9	8.30	8.40	0.638	336	weak
60/40	93.0	6.92	7.06	0.566	-	very weak
50/50	92.3	5.61	5.67	0.584	-	none

*Measured for solutions in p-chlorophenol at 45°C, except for the first polymer
which was measured in trifluoromethanesulfonic acid at 30°C.

TABLE 3. Synthesis and Properties of CHQ/BPM Copolyesters

Monomers/moles CHQ/BPM	Yield, wt.%	n_{inh} *	M.P.°C	Stir-Opalescence
70/30	98.3	0.630	304	very strong
50/50	97.1	0.407	304	strong
40/60	92.5	0.433	296	strong
30/70	96.7	0.718	-	none

*Measure for solutions in p-chlorophenol at 45°C.

TABLE 4. Synthesis and Properties of CHQ/ODP Copolyesters

Monomer/mole CHQ/ODP	Yield, wt.%	n_{inh} *	M.P.,°C	Stir-Opalescence
70/30	95.4	0.433	298	very strong
50/50	97.8	0.484	327	strong
40/60	95.9	0.401	380	strong
30/70	94.0	0.395	389	weak

*Measured for solutions in p-chlorophenol at 45°C

TABLE 5. Synthesis and Properties of CHQ/TDP Copolyesters

Monomers/mole CHQ/TDP	Yield wt.%	n_{inh} *	M.P.°C.	Stir-Opalescence
70/30	98.3	0.503	314	strong
50/50	97.2	0.709	339	strong
40/60	99.0	0.655	348	weak

*Measured for solutions in p-chlorophenol at 45°C.

TABLE 6. Synthesis and Properties of CHQ/SDP Copolyesters

Monomer/mole CHQ/SDP	Yield, wt.%	η_{inh}*	M.P.,°C.	Stir-Opalescence
68/15	99.8	-	334	very strong
70/30	98.0	0.439	342	strong
60/40	96.6	0.479	376	strong
50/50	91.9	0.315	367	weak
40/60	98.8	0.440	-	none

*Measured for solutions in p-chlorophenol at 45°C.

TABLE 7. Synthesis and Properties of CHQ/BP Copolyesters

Monomer/mole CHQ/BP	Yield, wt.%	η_{inh}*	M.P.,°C	Stir-Opalescence
70/30	99.3	0.107	340	strong
50/50	99.1	0.163	354	strong
30/70	99.3	0.224	390	strong

*Measured for solutions in trifluoromethanesulfonic acid at 30°C; it is possible that these polymers underwent hydrolysis during characterization.

TABLE 8. Synthesis and Properties of CHQ/RES Copolyesters

Monomer,mole CHQ/RES	Yield, wt.%	η_{inh}*	M.P.,°C	Stir-Opalescence
85/15	97.7	-	334	very strong
70/30	98.0	0.363	330	very strong
50/50	98.2	0.422	-	strong
40/60	99.4	0.476	-	weak
30/70	99.4	0.390	337	none

*.

TABLE 9. Synthesis and Properties of MHQ/BPA Copolyesters

Monomer,mole MHQ/BPA	Yields wt.%	η_{inh}*	M.P.,°C	Stir- Opalescence
100/0	96.2	-	371	very strong
85/15	95.9	0.491	369	strong
70/30	96.4	0.604	-	very weak
50/50	92.7	0.496	-	none

*Measured for solutions in 60 phenol/40 tetrachloroethane (w/w) at 30°C.

TABLE 10. Synthesis and Properties of
50 MHQ/50 Bisphenol (moles) Copolyesters

Bisphenol	Yield, wt.%	η_{inh}*2	M.P.,°C	Stir- Opalescence
BPA	92.7	0.496	-	none
BPM	98.5	0.670	289	strong
ODP	92.8	0.524	350	strong
TDP	88.0	0.410	334	strong
SDP	94.3	0.535	354	weak
DBP*1	94.3	0.438	399	strong
EP	98.6	-	-	strong

*1. 4,4'-dihydroxybenzophenone, X is -CO- .

*2. Measured for solutions in p-chlorophenol at 45°C except for the BPA
copolyester, which was measured for a solution in 60 phenol/40
tetrachloroethane (w/w) mixture at 30°C.

TABLE 11. Maximum Amount of Each Bisphenol Which Could be
Copolymerized Without Complete Destruction of the
Liquid Crystallinity of the CHQ Copolyester.

Bispheol	Maximum Amount, mole %
BPA	40
SDP	50
BPM	60
TDP	60
RES	60
ODP	70
BP	100

Figure 1. Photomicrographs of the Quenched Melts of CHQ/BPA Copolyesters
(Photograph spans a sample length of 440 um)

(a) Photomicrograph of Poly(chloro-p-phenylene terephthalate)
(Magnification x 320)
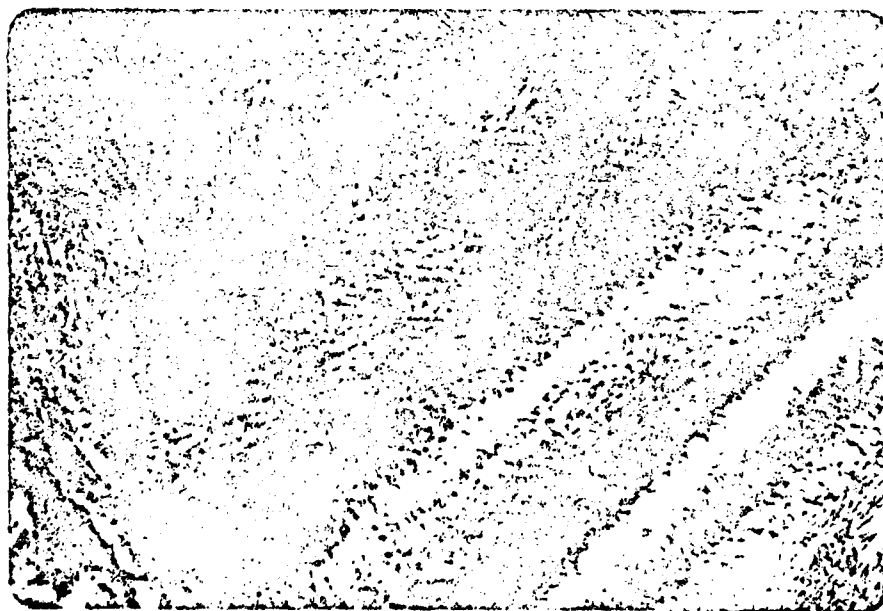
(b) Photomicrograph of 90CHQ/10 BPA Copolyester
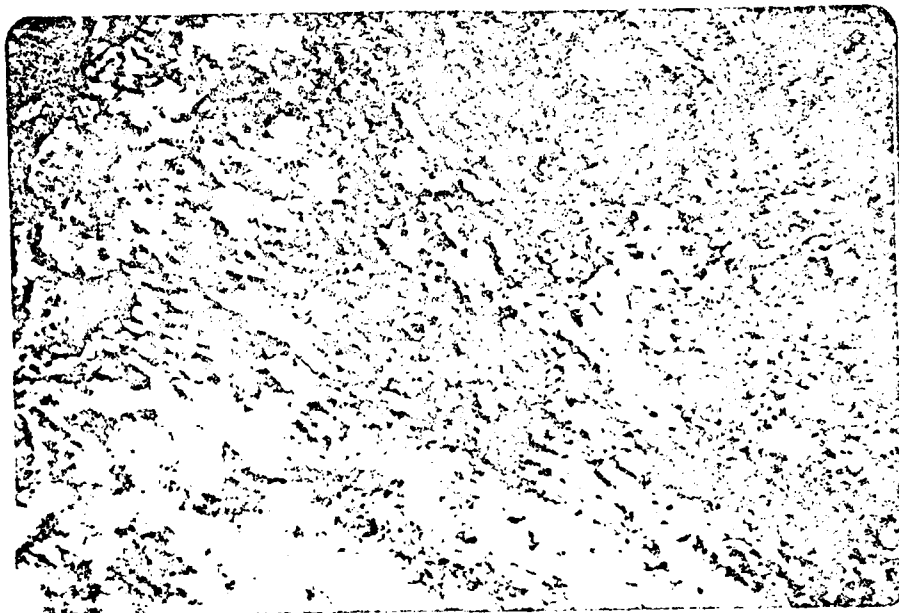
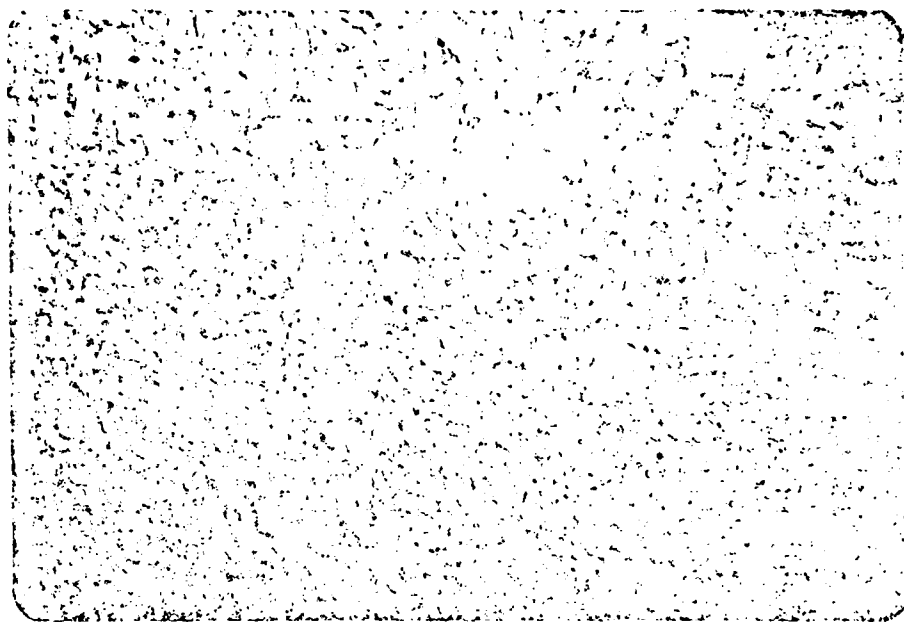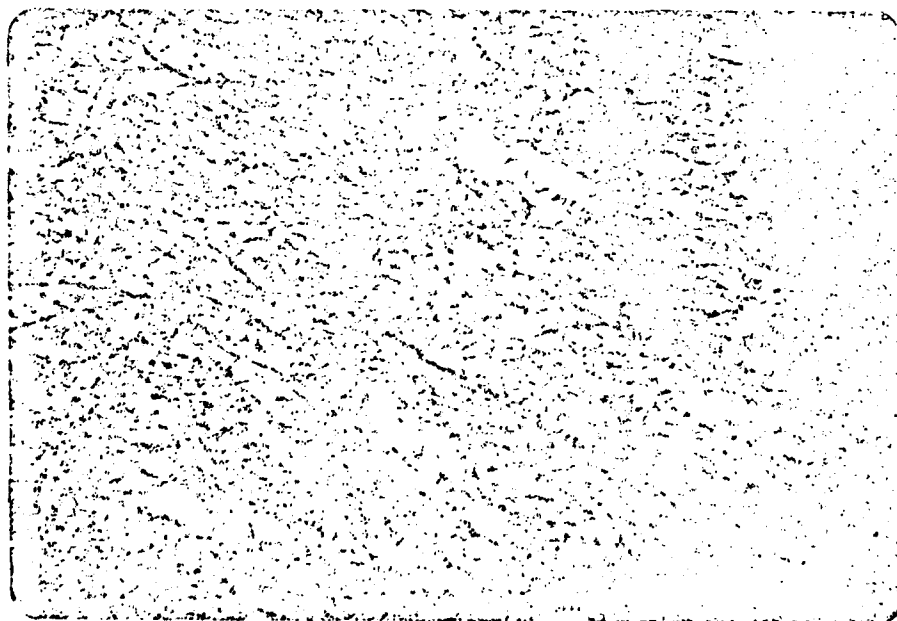(c) Photomicrograph of 70 CHQ/30 BPA Copolyester
     (Magnification x 320)
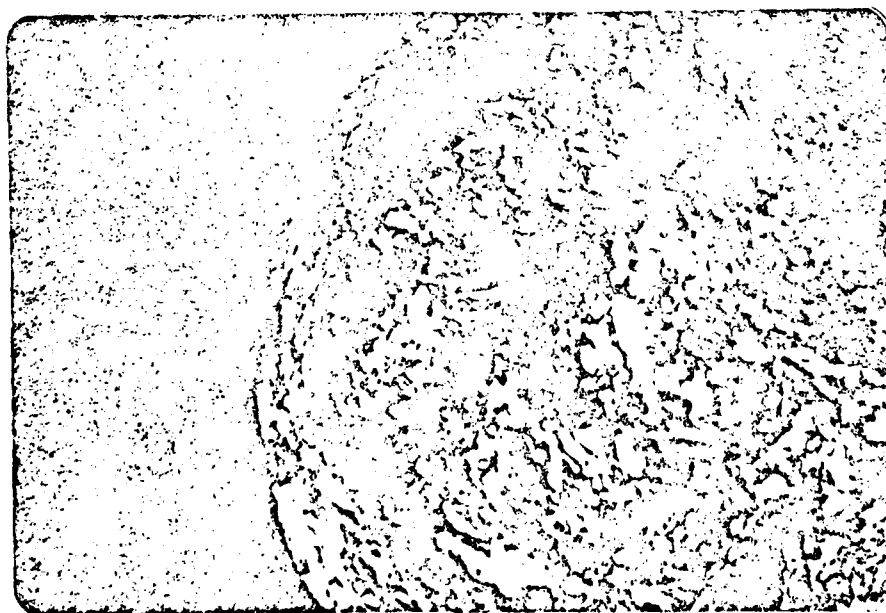
(d) Photomicrograph of 60 CHQ/40 BPA Co
     (320)

Figure 2. Photomicrographs of the Quenched Melts of 70 CHQ/30 CDP and
            70 CHQ/30 BP Copolyesters (Photograph spans a sample length of
            440 μm).

(a) Photomicrograph of 70 CHQ/30 CDP Copolyester
     (Magnification x 320)

(b) Photomicrograph of 70 CHQ/30 BP Copolyester
     (Magnification x 320)

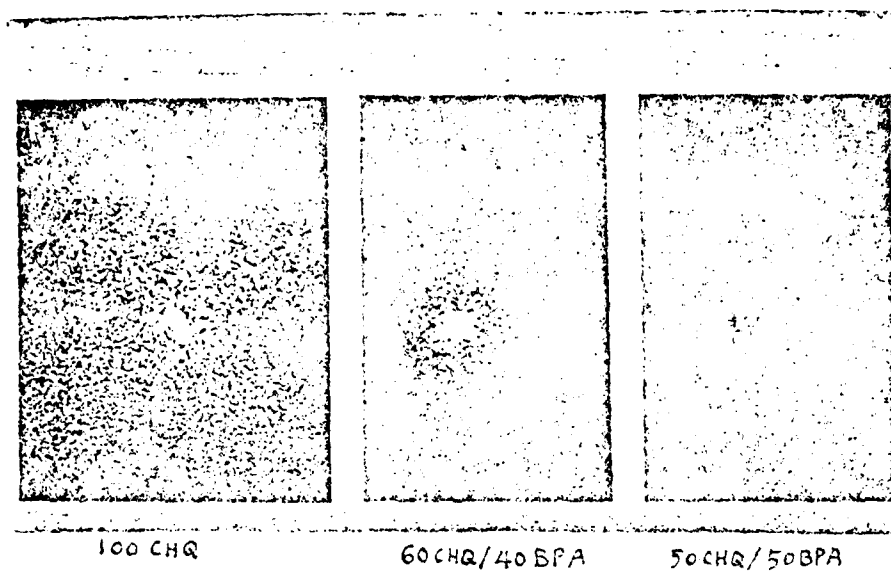Figure 3.   Small Angle Light (H_v) Scattering Patterns of
CHQ/BPA Copolyesters

100 CHQ   60 CHQ/40 BPA   50 CHQ/50 BPA

Figure 4. Small Angle Light (H_v) Scattering Patterns of CHQ/SDP Copolyesters

70 CHQ / 30 SDP   60 CHQ/40 SDP

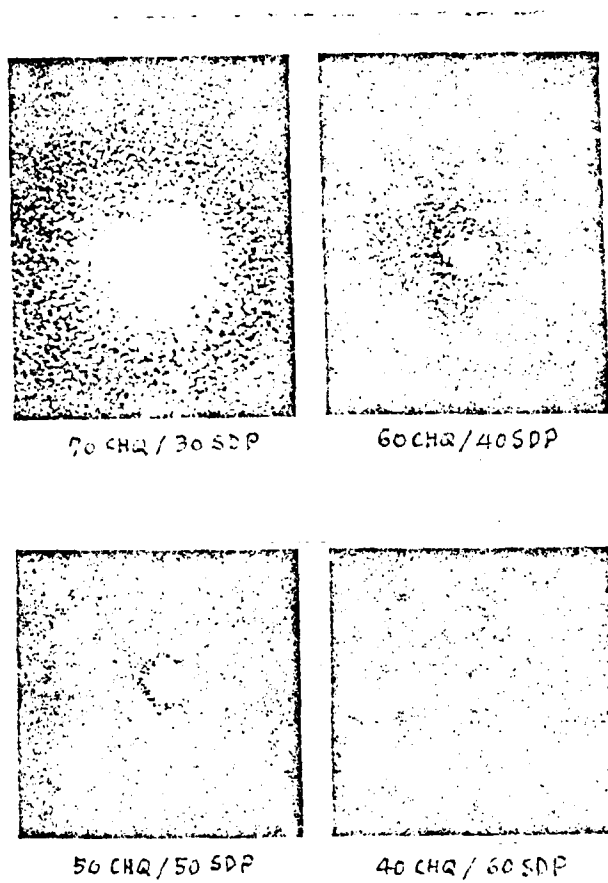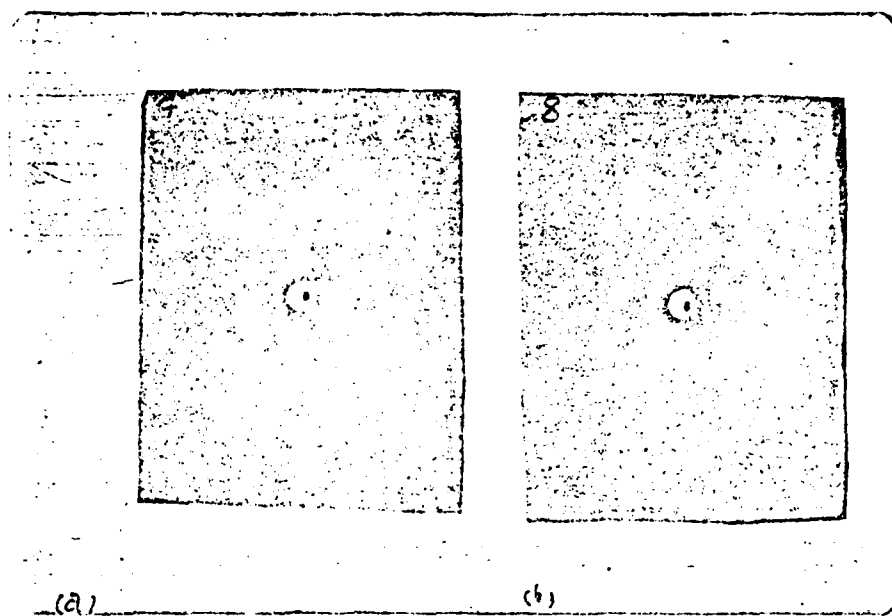50 CHQ / 50 SDP   40 CHQ / 60 SDP

Figure 5. Wide Angle X-Ray Diffraction Patterns of
70 CHQ/30 ODP Copolyester

(a) Diffraction by the Original Sample

(b) Diffraction by the Quenched Sample

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